Advanced Composite Coatings for Industries of the Future

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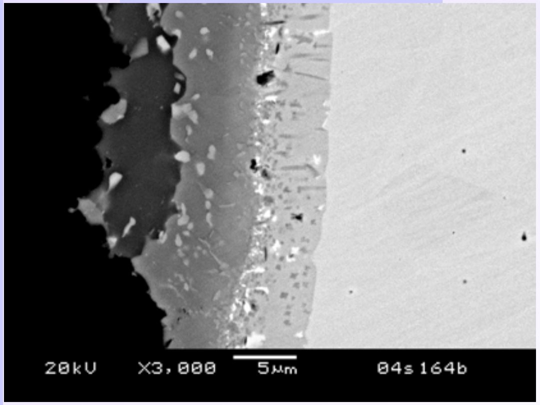
5-year Project 2001-2006, $1.35M

SRI $100K/yr, UW $75K/yr, UCF $50K/yr, PNNL $175K/yr.

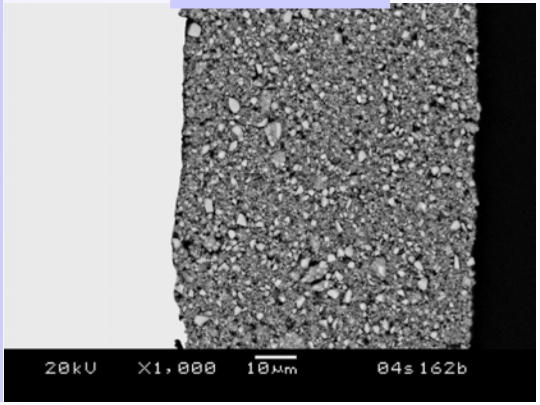
Project Summary

- **Goal**
  - Develop low-cost coatings for prevention of high-temperature corrosion of metals and ceramics.
- **Challenge**
  - Provide protection of high CTE metals and alloys at 700˚C to 1000˚C in oxidizing and reducing environments.
    - Specifically, prevent 316SS metal dusting in reformers.
- **Benefits**
  - Energy savings of 160 trillion Btu/year in 2010 assuming a 5% increase in efficiency.
    - Higher temperature operation and use of low-cost alloys.
    - Inexpensive and simple processing of coatings.
- **FY05 Activities:**
  - Optimize coating formulation and coating strategy.
  - Improve coating sealing.
  - Enhance understanding of coating and coating-substrate interactions.
  - Testing of coatings under realistic conditions.
  - Development of commercialization plans.
  - Pursue possible patent applications.

Aluminide Coating



SiC Coating



Barrier-Pathway Approach

- **Barrier**
  - Lack of low-cost coating to prevent carburization of steels in steam-reformer environments.
- **Pathway**
  - Low-cost, paintable, polymer-based coatings.
    - Corrosion resistant ceramic coatings.
    - Aluminide diffusion coatings.
- **Critical Metrics**
  - Survive processing at 800-1000˚C on high CTE steels.
    - Thermal cycling (10x) to 800˚C.
    - 1000 h at operating conditions (temperature and environment).
- **Benefits** (based on 5% increase in efficiency)
  - Energy savings of 160 trillion Btu/yr.
  - Savings of 3.8 MMTCE.

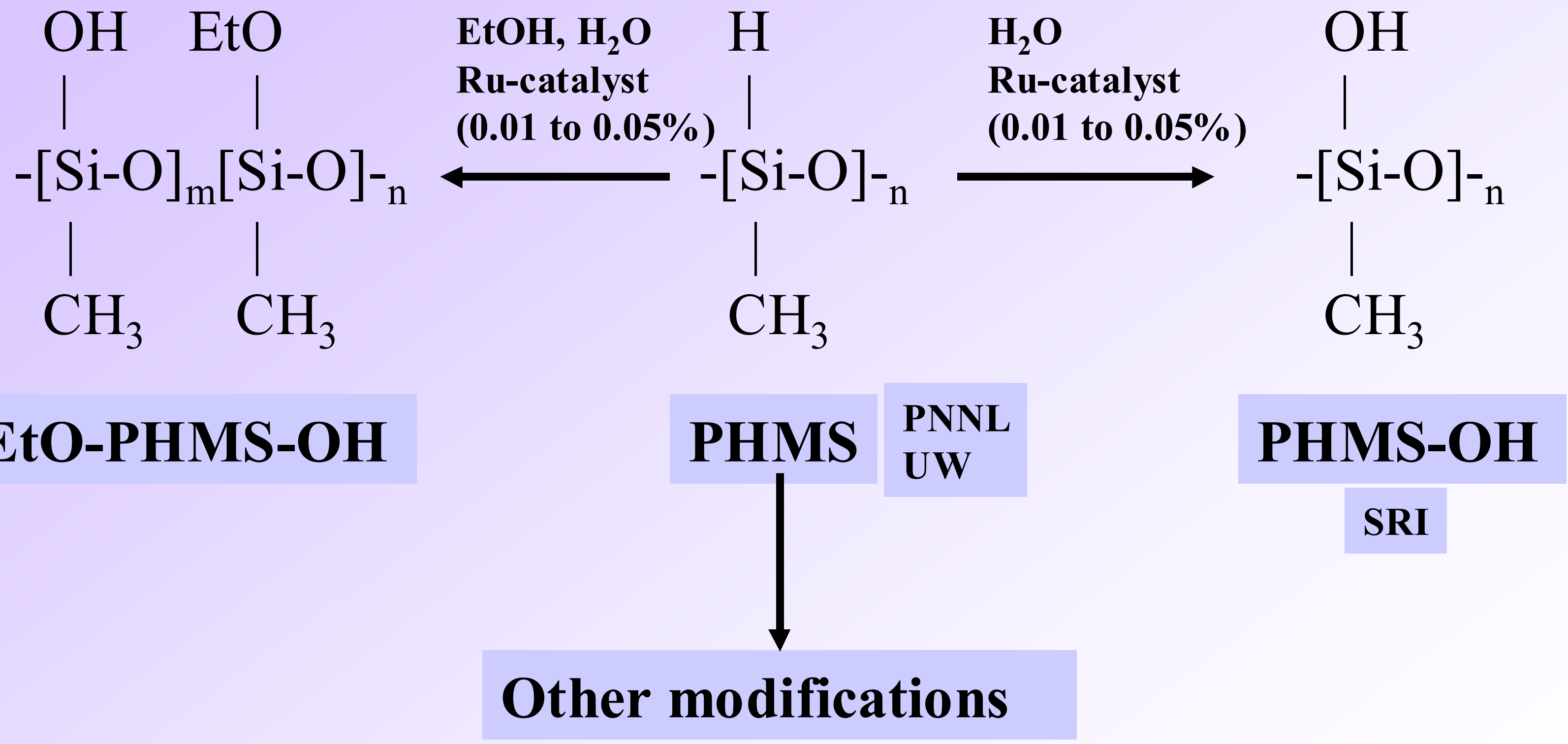
Technical Approach

- Polysiloxane polymers convert to Si-O-C-N materials, which are ideal for low-cost protective coatings.
  - A very inexpensive polymer precursor (PHMS) is being used (5-10 $/kg) after switching from polysilsesquioxanes.
  - PHMS chemistry is robust for organic attachments and curing reagents that can be used to control the final coating chemistry.
  - Reactive and inert metal/ceramic fillers to accommodate differential shrinkage, constrained sintering stresses, and thermal expansion.
  - Multilayer coatings for graded CTE and specific protection in a desired environment.
- Coating processing tailored for microstructure control.
  - Ceramic coatings and diffusion aluminides have similar processing.
  - Coating application is by painting: dipping, brushing, spraying.
- Coating characterization and testing.
  - Microstructural and chemical.
  - Mechanical Testing (Adhesion).
  - Thermal cycling.

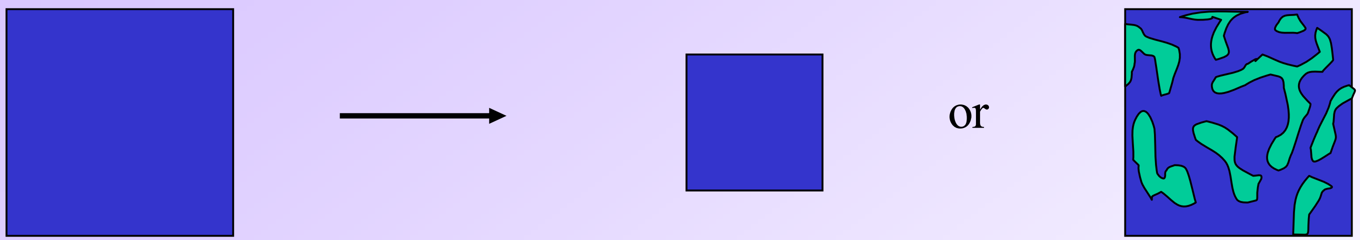
Project Highlights and Accomplishments

- A novel, diffusion aluminide coating process has been developed at PNNL.
  - Does not require hot-dipping, pack cementation, or fluidized bed CVD.
- Two ceramic-filled coatings have been developed (SiC at PNNL and $TiSi_2$ at UW) that survive 10-cycles to 800˚C on 316SS and 100 h at 800˚C.
- A novel 316SS-flake coating has been developed at SRI to grade high-CTE metals to ceramic outer seal coatings.
- Further development of coatings containing small and large fractions of Al flakes (as reactive fillers) has been performed at PNNL and SRI.

PHMS Polymer Chemistry



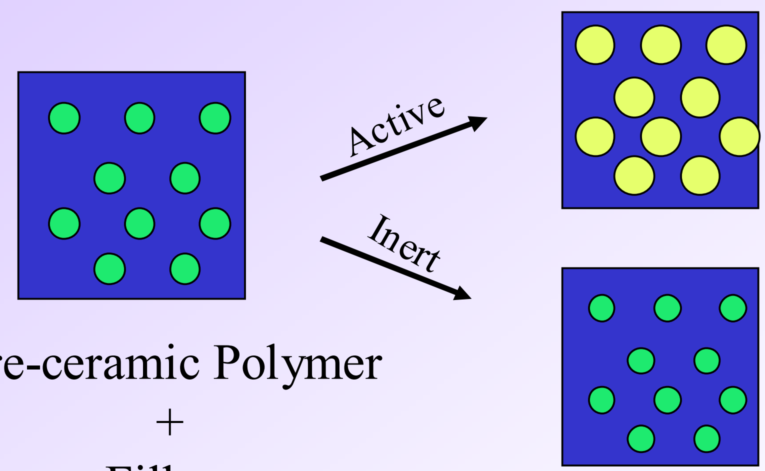
Role of Fillers in Shrinkage Control



Pre-ceramic Polymer

up to 50% volume shrinkage

porosity



Pre-ceramic Polymer
+
Fillers

Filler reacts to form an expanded phase and compensate for polymer shrinkage

Filler reduces volume of polymer and associated shrinkage

Design of Composite Coatings

Pre-Ceramic Polymer Matrix

- Ease of processing (painting, spraying, dipping)
- Wetting and good bonding to surfaces
- Low temperature conversion to ceramic
- Protective final compositions

Powder Fillers

- Control shrinkage during pyrolysis (prevent cracking and delamination)
- Control of microstructure and mechanical properties
- Control of thermal expansion mismatch to substrate
- Control of interface bonding
- Improvement of hermeticity

Advanced Composite Coatings

- Al/Alumina powder mixtures
  - Approximately 40 to 60 v/o powder loadings (Al/Alumina equal ratio)
  - Al-flake, 1-2 μm alumina powders.
  - Alumina nanopowders.
- SiC powder
  - 0.7 μm α-SiC powder at 40 to 60 v/o loading.
- $TiSi_2$ powder mixtures
  - Alloyed powders attrition milled to < 5 μm and 40 to 60 v/o loading.
- Stainless steel powder mixtures and multilayer coatings.
  - 316SS flake, 30-50 μm, 40 to 60 v/o.

Simple Coating preparation

- Mix powders, polymer, solvents in roller-mill.
- Dip, spray, paint on substrates.
- Pyrolyze at 800˚C to 1000˚C in air, nitrogen, or argon.

Ease of Coating Application

Polymer/filler slurry can be applied like a paint in air at ambient conditions: Dipping, spraying, painting.

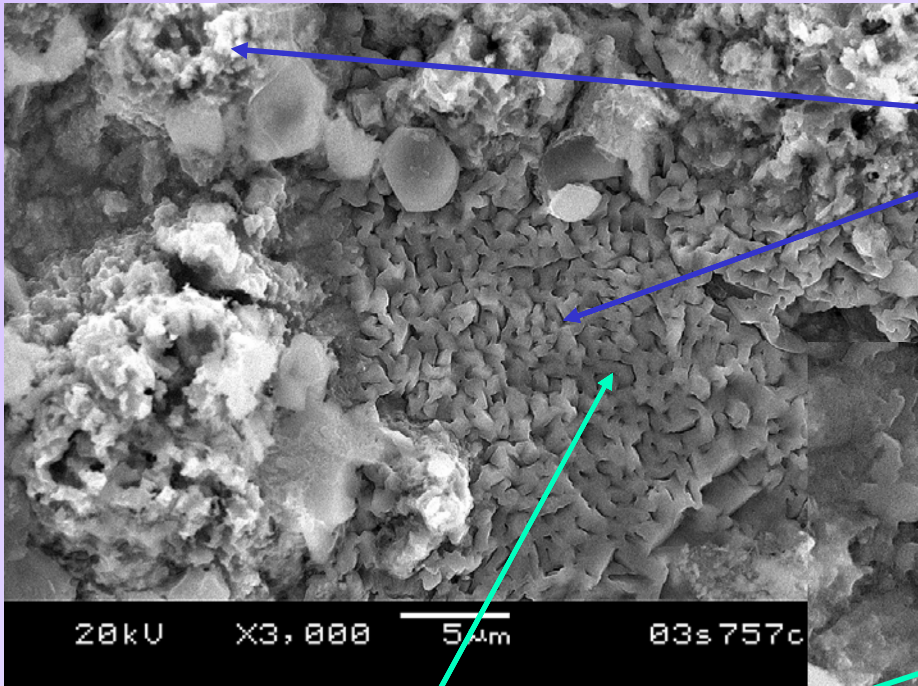
Spraying is performed in a hood using compressed air and thinned slurry. Thinning uses same solvent as is used to control viscosity for dipping but requires 2X solvent for spraying.

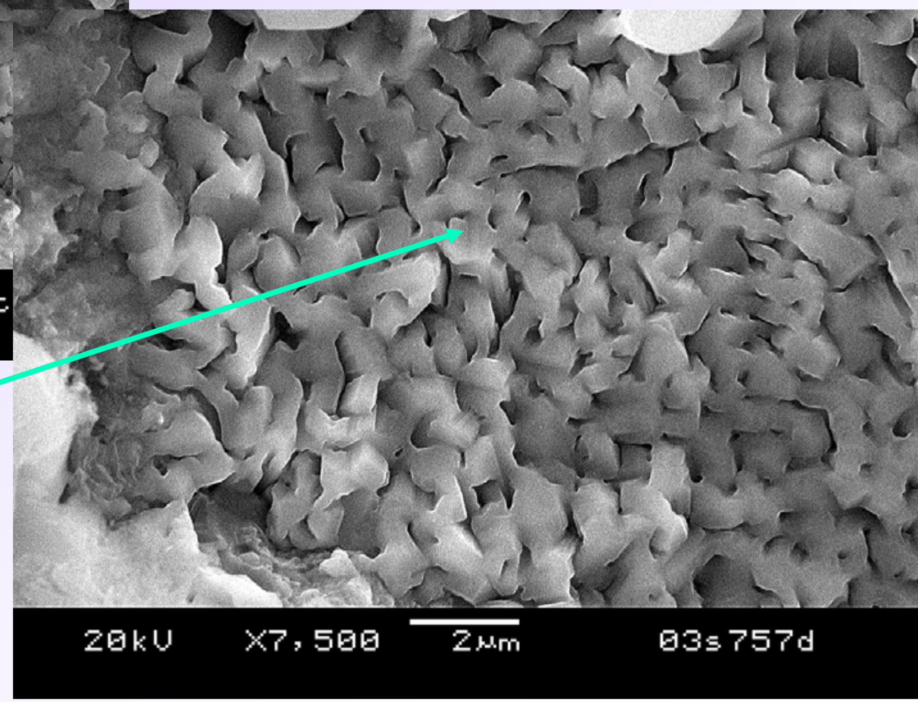
Summary of Coatings on Metals
(316SS and 430SS)

- Al/Al_2O_3 coatings react to from FeAl regions on steels.
  - Novel slurry-based diffusion aluminide coatings.
  - Nodules and interwoven FeAl regions on 316SS.
  - Extremely adherent and protective.
- SiC coatings adherent and continuous.
  - "packed" powder appearance. (Hermeticity?)
  - Survives repeated thermal cycling to 800˚C.
- $TiSi_2$ coatings adherent and continuous.
  - "packed" powder appearance. (Hermeticity?)
  - Survives repeated thermal cycling to 800˚C.
- Stainless steel flake coatings are adherent as underlayer.
  - Provide CTE match to 316SS and graded underlayer.
  - Adherent coatings to at least 1000˚C in argon and up to 800˚C in air.

SEM Image of Novel Diffusion Aluminide Coating (Al/Al_2O_3) on 316SS

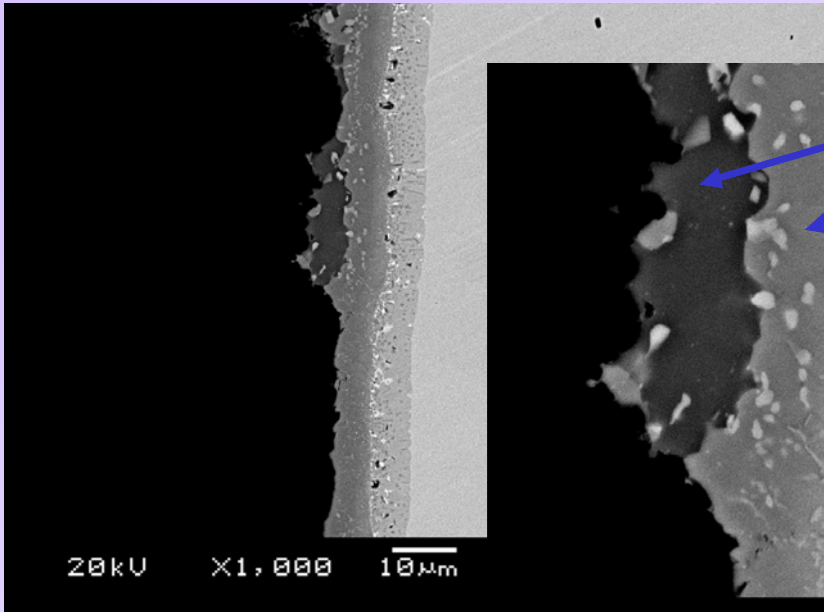
- "Dual Phase" coating.
- Nodular and glassy regions plus a metallic interwoven region.
- EDS & XRD reveals FeAl phase.

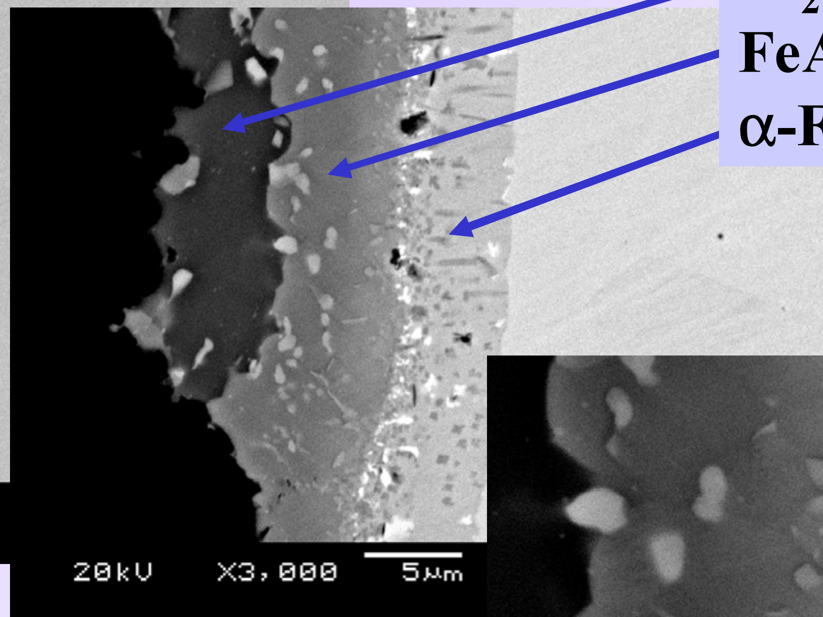


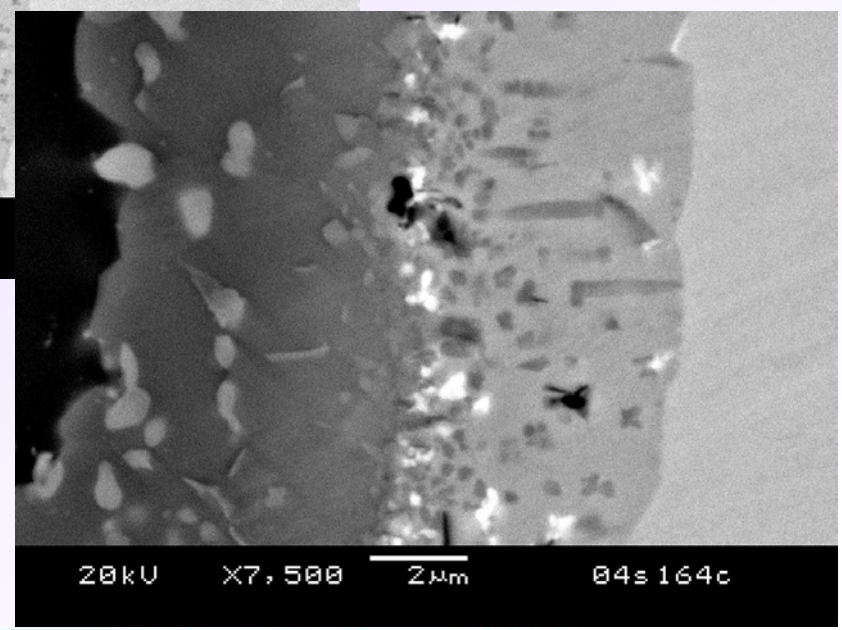


FeAl

Cross-section SEM of Diffusion Aluminide Coating on 316SS



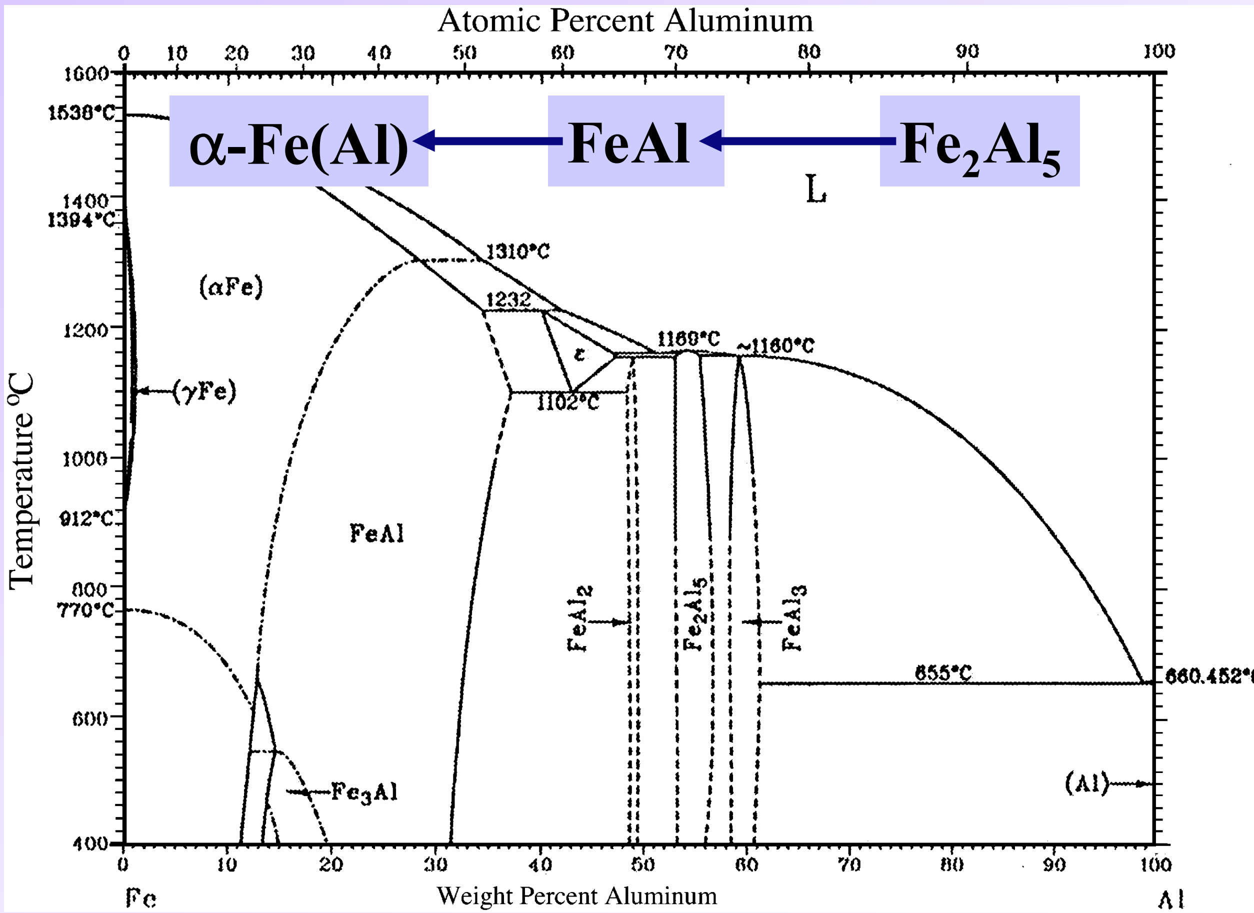




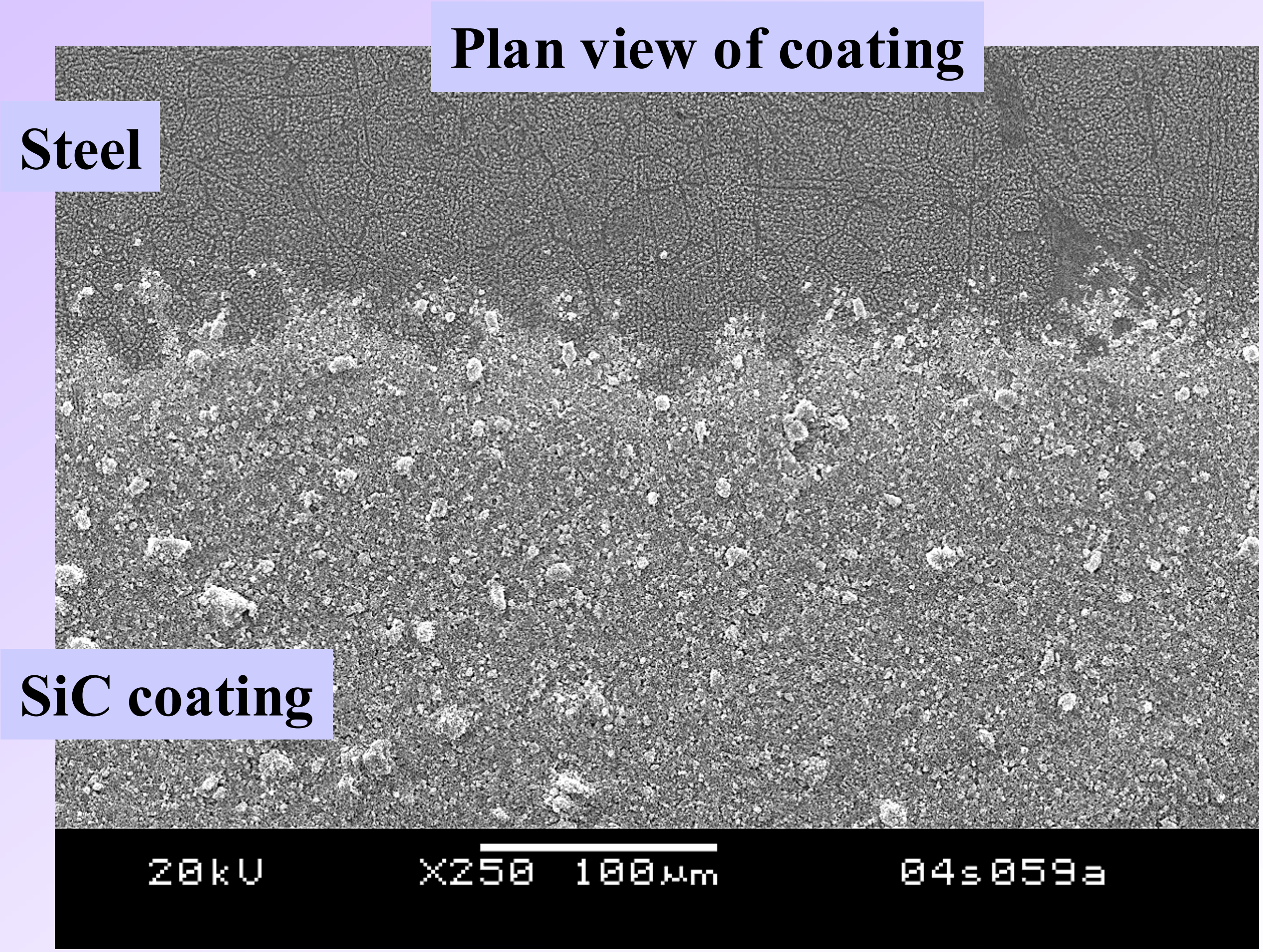
Coating is complex and TEM results will guide understanding.

AlFe Phase Diagram

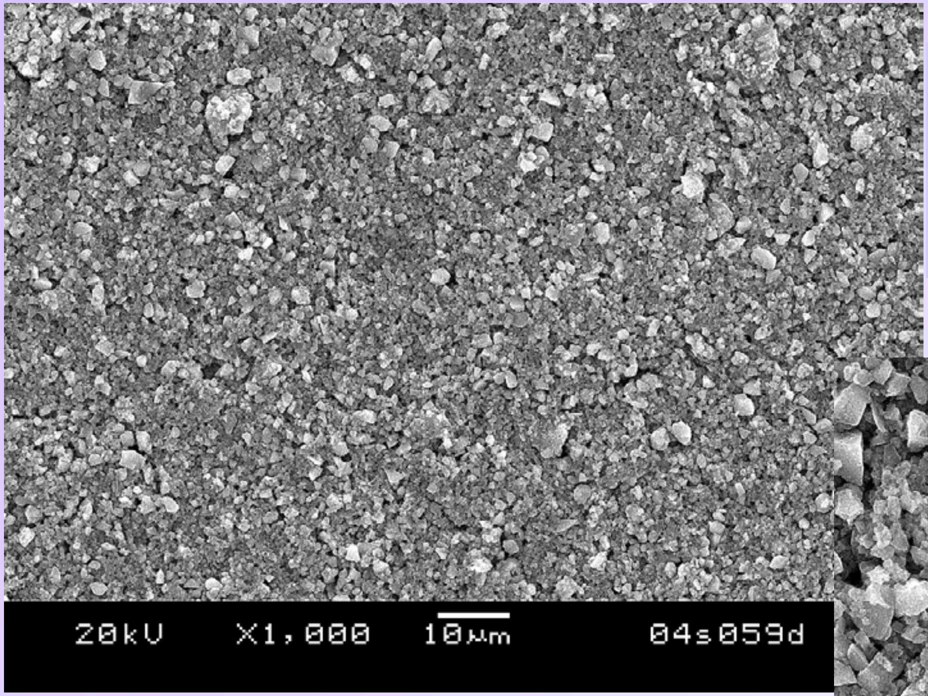
Al diffusion into steel (typical phase sequence)



SEM Image of SiC-filled coating on 316SS

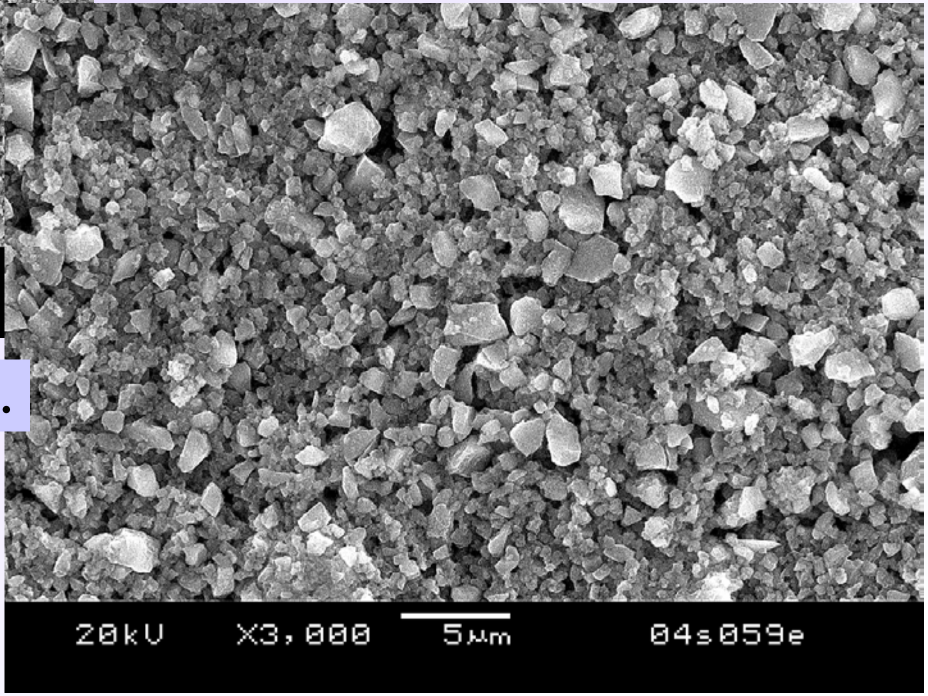


SEM Image of SiC-filled coating on 316SS

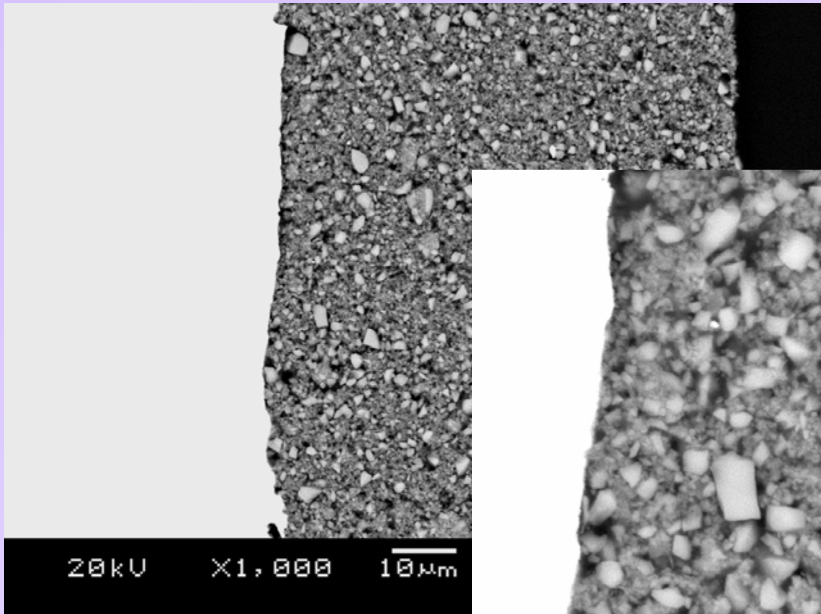


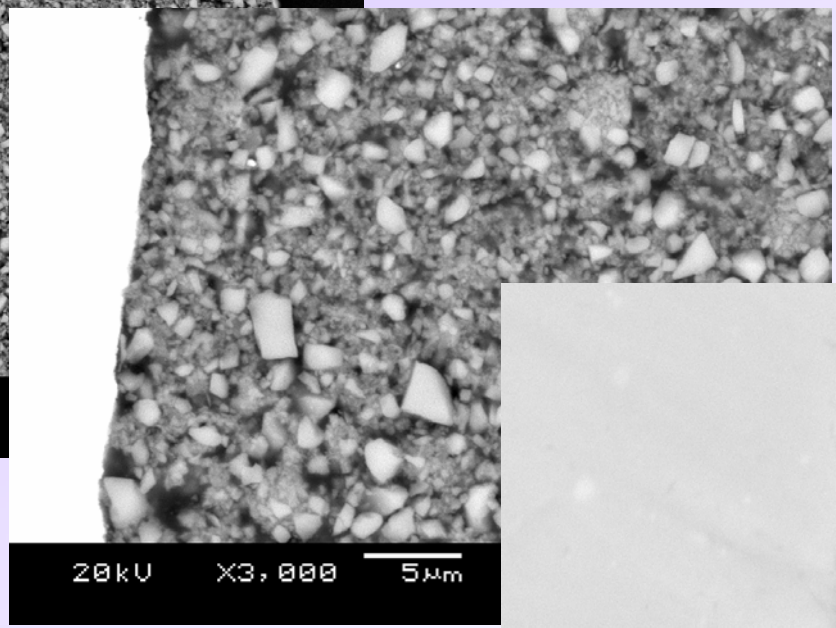
- Coating appears to be compliant particulate layer.
- Hermetic?

Plan views of SiC coating.

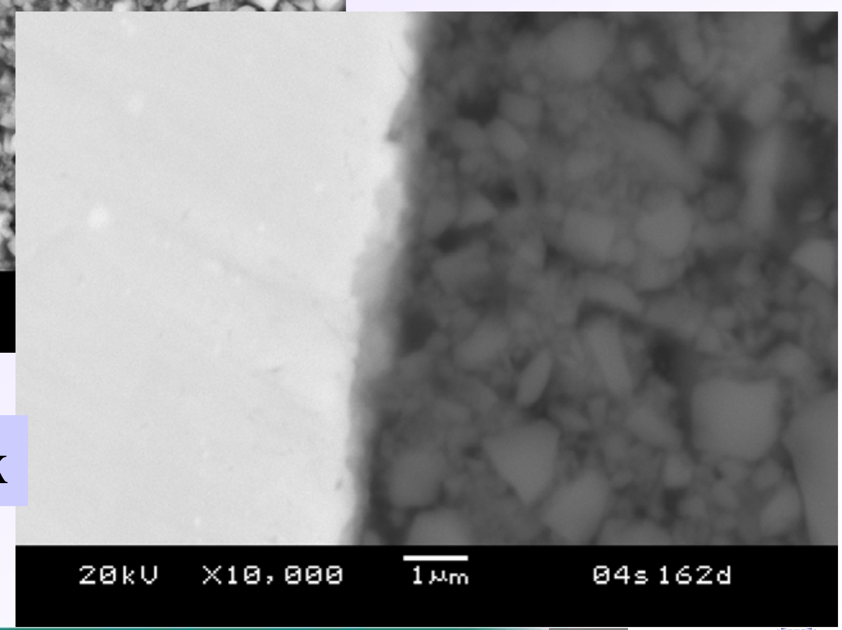


SiC coating (60 v/o) is thick, uniform, and adherent.



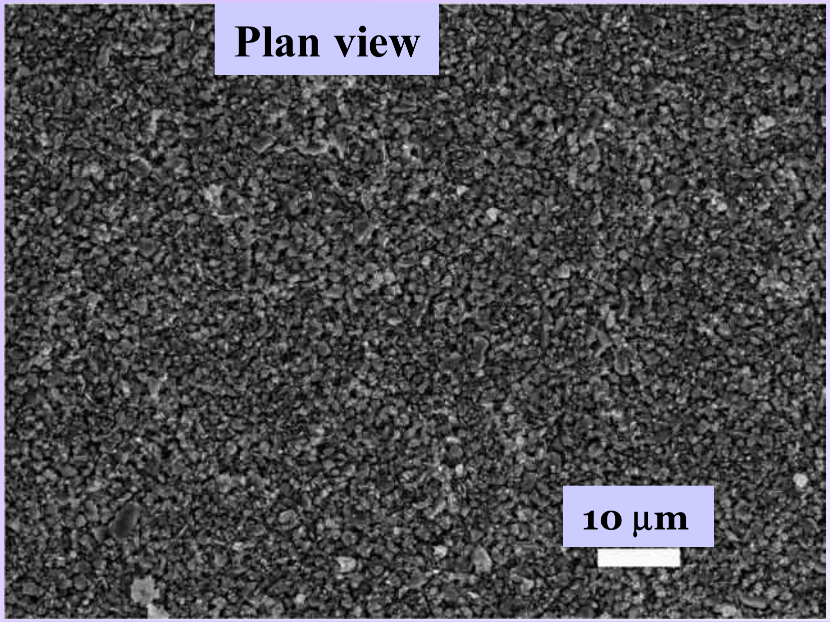


SiC cross-section views



SiC particles in glassy matrix

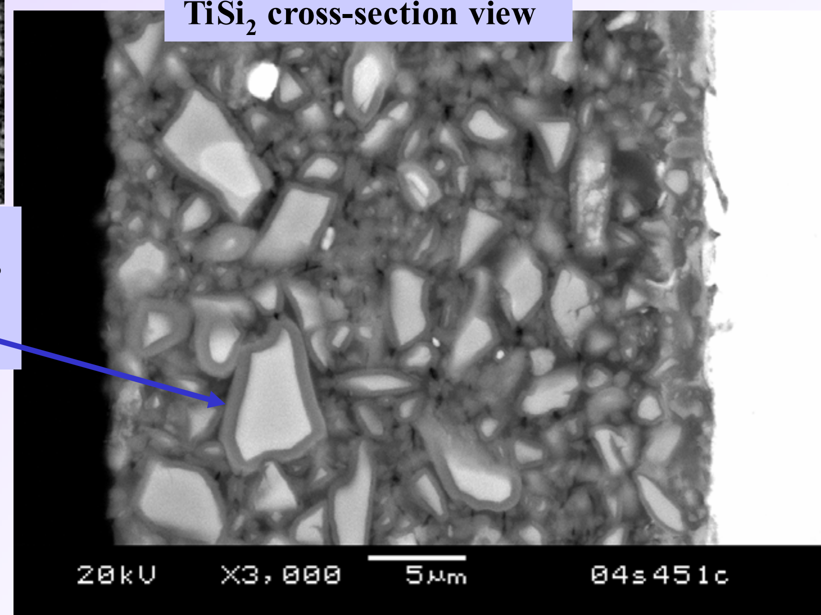
$TiSi_2$-filled Coating on 316SS



20 µm thick coating.
good adherence to metal.
Appears dense.

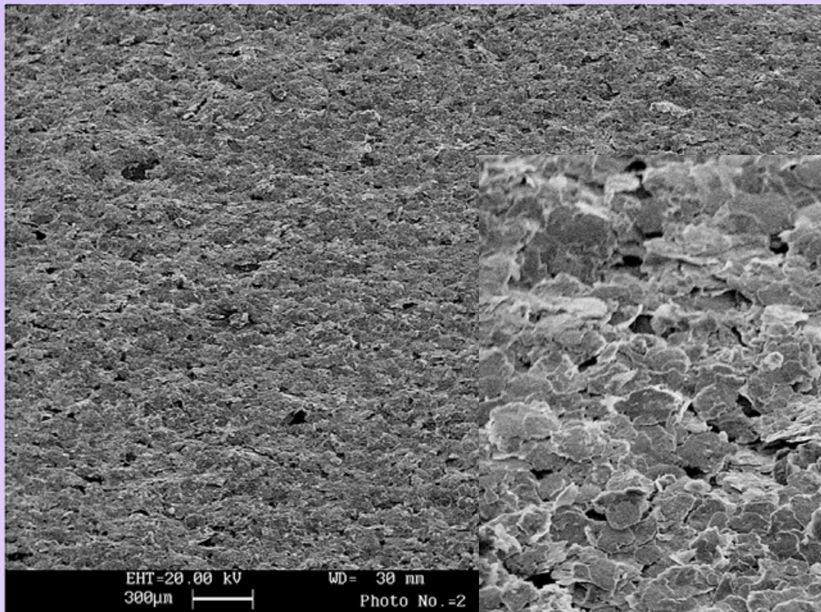
$TiSi_2$ particles in glassy matrix.
Partially converted to oxide.

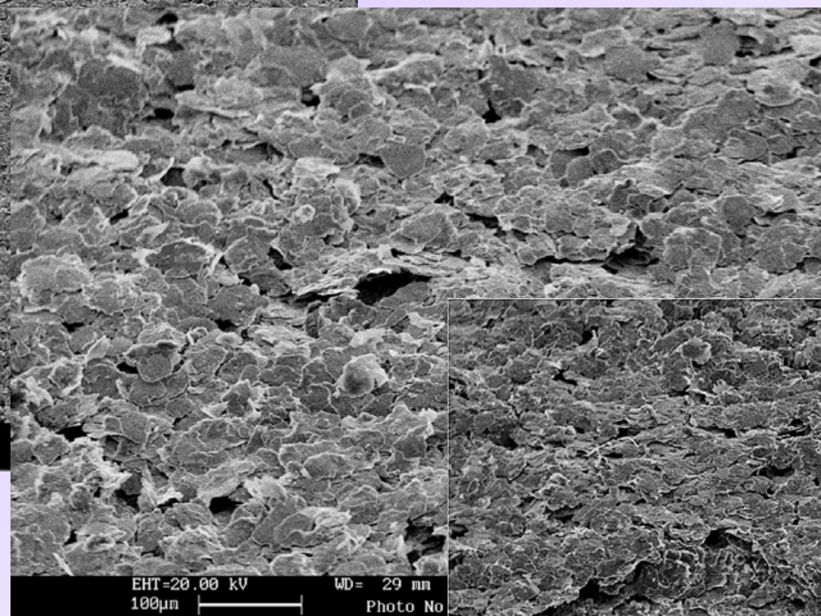
$TiSi_2$ cross-section view

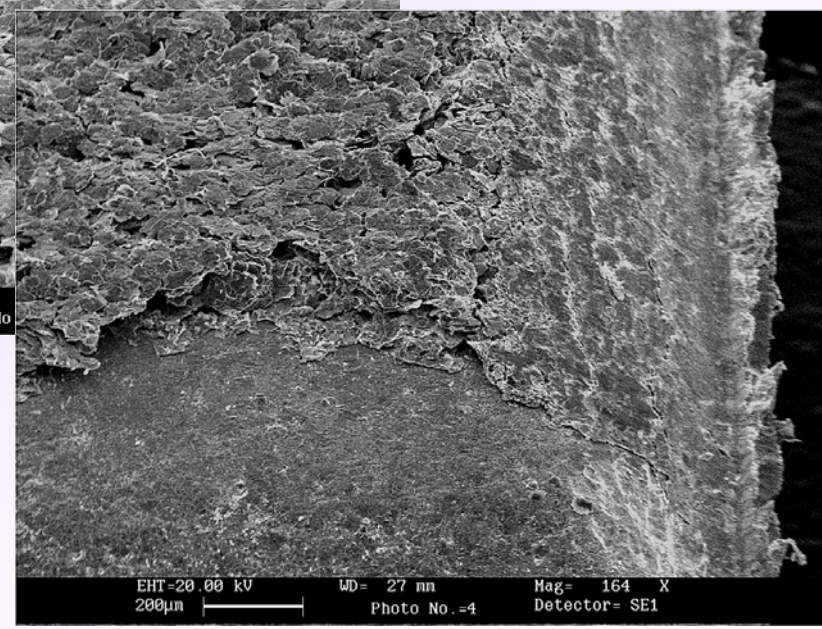


316SS-filled Coatings on 316SS

Designed to serve as graded underlayer for multilayer coating.







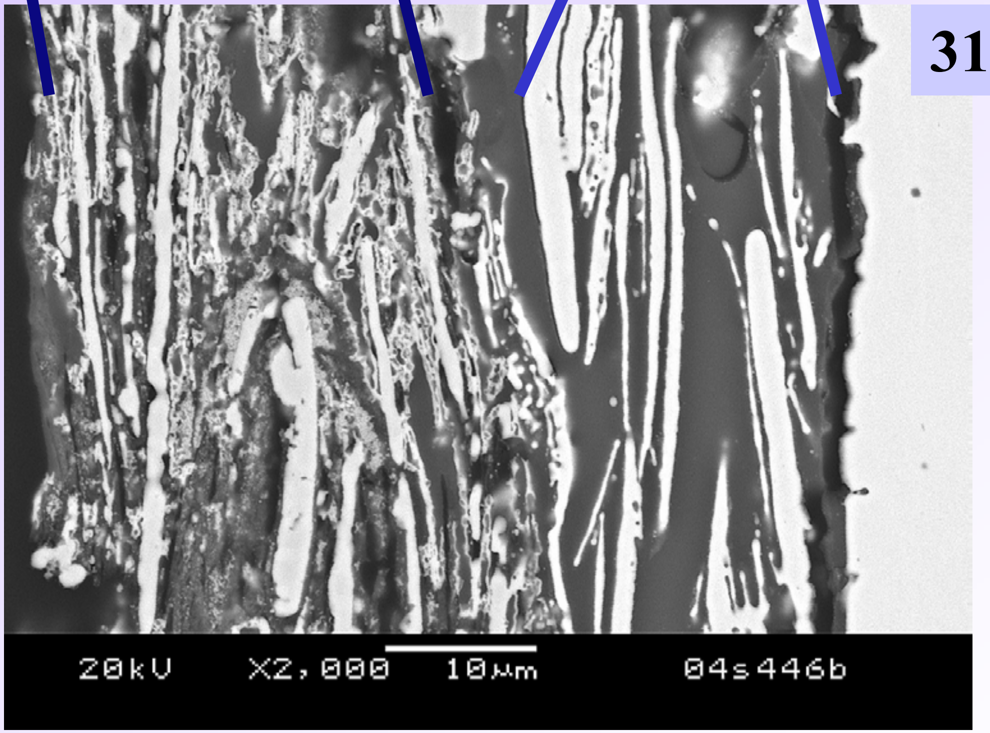
- **Stainless steel (SS316) flakes 40 v/o; PHMS-OH 60 v/o**
- **Coating bonds strongly.**
- **No cracking of the coatings.**
- **Areas with delaminated coating still maintain a coated film at the surface.**

Two-layer Coatings on 316SS

<u>Second layer:</u> 316SS flake – 25 v/o Al flake – 15 v/o; 1000˚C in Argon

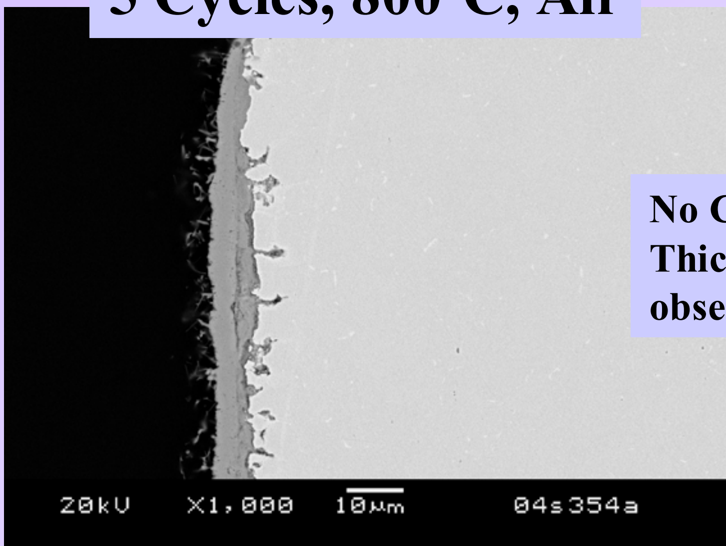
<u>First layer:</u> 316SS flake – 40 v/o; 1000˚C in Argon

316SS

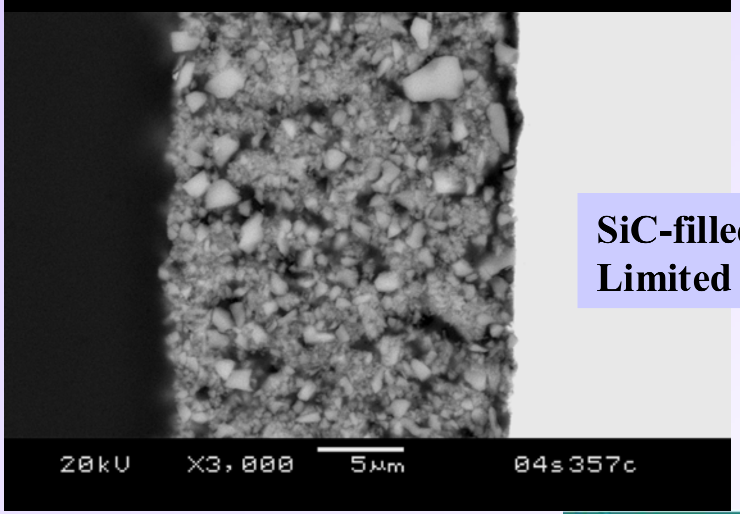


Cyclic and Static Oxidation Testing: SiC Coating

5 Cycles, 800°C, Air

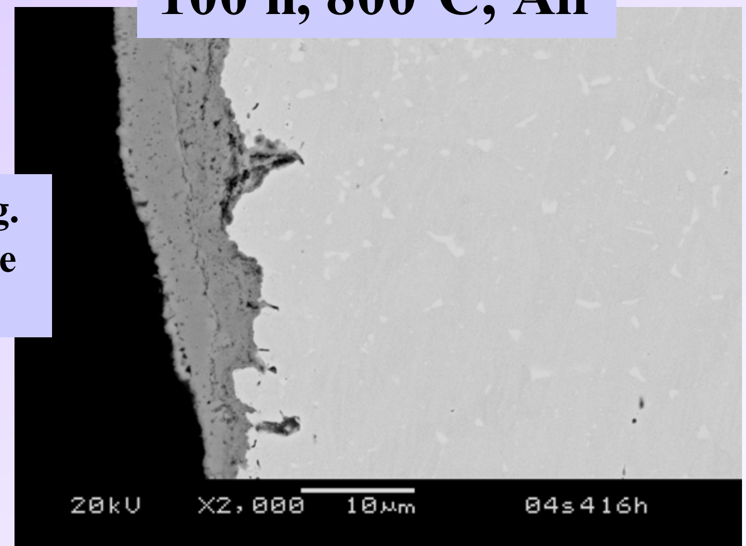


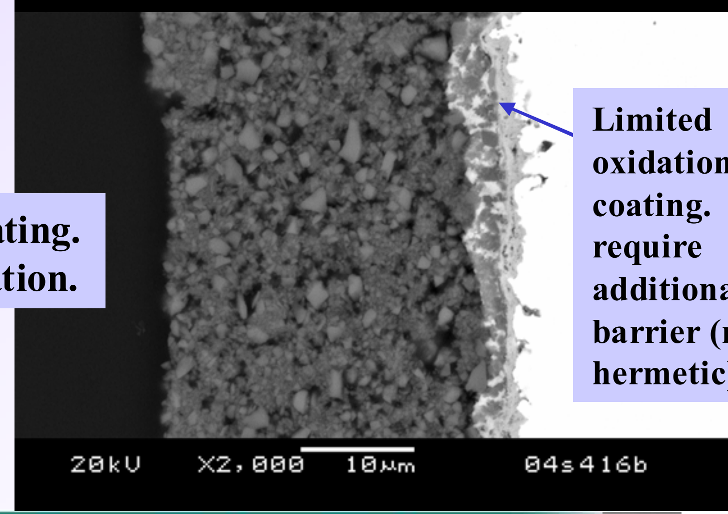
No Coating. Thick oxide observed.



SiC-filled Coating. Limited oxidation.

100 h, 800°C, Air

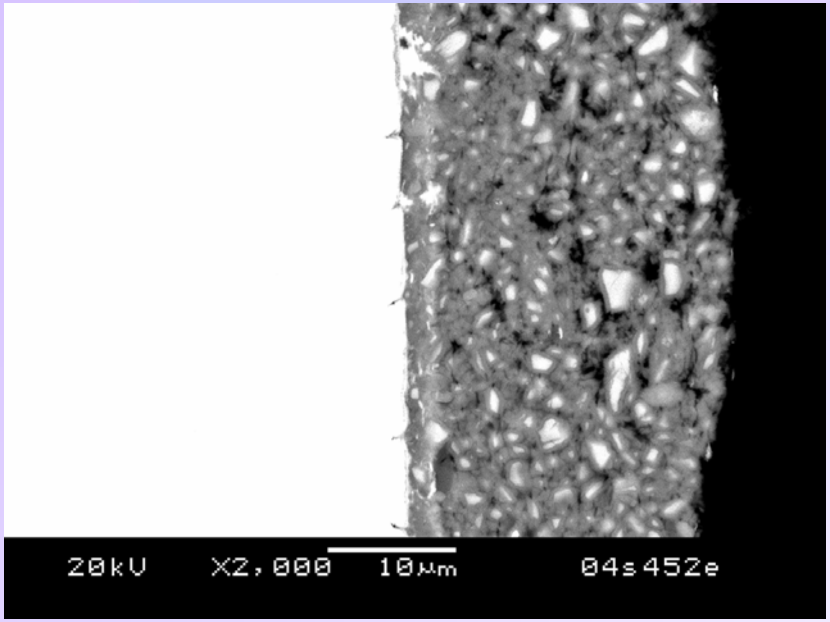




Limited oxidation under coating. May require additional barrier (non-hermetic)

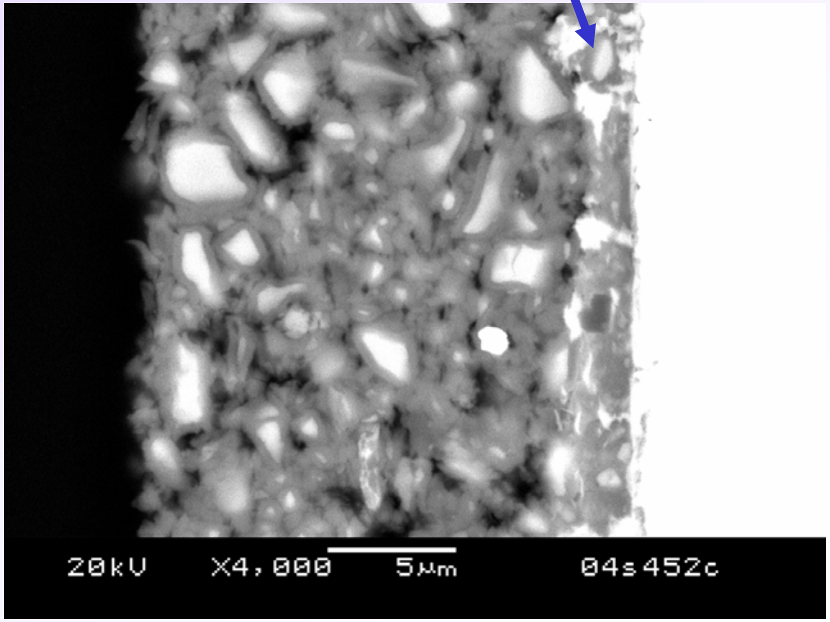
Cyclic and Static Oxidation Testing: $TiSi_2$ Coating

5 Cycles, 800°C, Air



$TiSi_2$-filled Coating.
Limited oxidation.

Limited oxidation under coating.
May require additional barrier
(non-hermetic)



Future Plans for FY05

- Work with industrial partner to insure that coatings are tested and evaluated properly.
  - Complete oxidation and cyclic exposure testing (started).
  - Develop method to test coatings in Steam Methane Reformer (SMR) environment (simulated).
- Develop method to seal porous or compliant powder coatings for hermeticity.
  - Explore PHMS seal coat for SiC-coating.
- Develop topcoat layer for 316SS-powder coating underlayer.
- Measure coating and interfacial mechanical properties.
- Commercial implementation path.

Commercial Implementation
Versatile Robust Coatings at Low Cost

PHMS-OH
7-14 $/Kg

PHMS
5-10 $/Kg

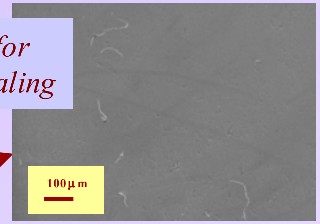
RO-PHMS-OH
5-10 $/Kg

Ceramic powder fillers
3-20 $/Kg

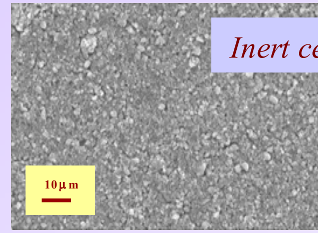
Reactive fillers
3-20 $/Kg

Attributes
Low cost "paints"
High temperature (>800°C)
Corrosion and chemical resistance
Large and complex surface area
Low maintenance
Energy Saving
Infrastructure saving
Energy production

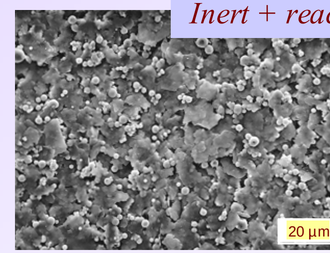
Unfilled thin films for planarization and sealing

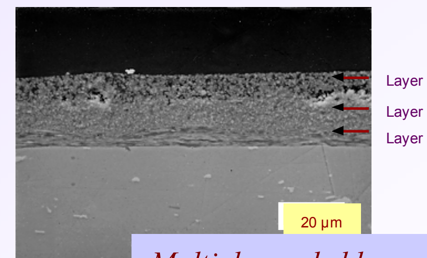


Inert ceramic filled

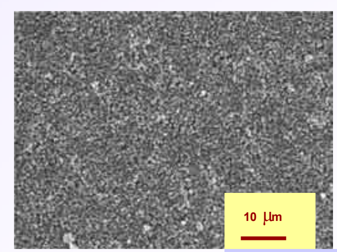


Inert + reactive filled

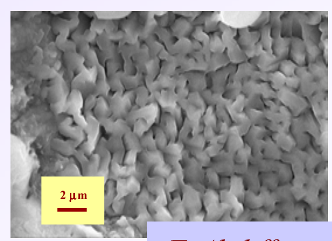




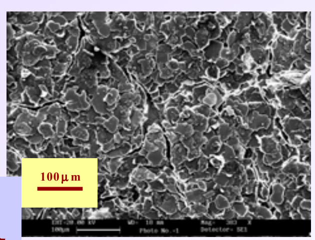
Multiple graded layers



Reactive metal filled



FeAl diffusion coatings



SS composite CTE matching

Implementation Plans

Carburization Resistance Coating Market

- Hydrogen economy
  - 80% of H_2 volume produced by SMR (Syngas)
  - AIR PRODUCTS alone – 35 SMR plants
  - Coal and Biomass gasification plants
    - 160 plants worldwide in 2000
    - Production equivalent to 770,000 oil barrels per day
  - Major uses of Syngas (H_2/CO) in production of
    - Ammonia
    - Methanol
    - Oxo-alcohols (for detergents)
    - Fischer Tropsch (Syngas to hydrocarbons)

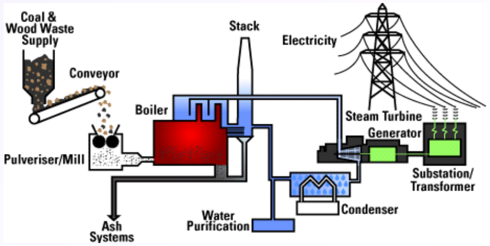
Growing volume maturity

Lower H_2/CO ratio
Higher carburization problem

Implementation Plans

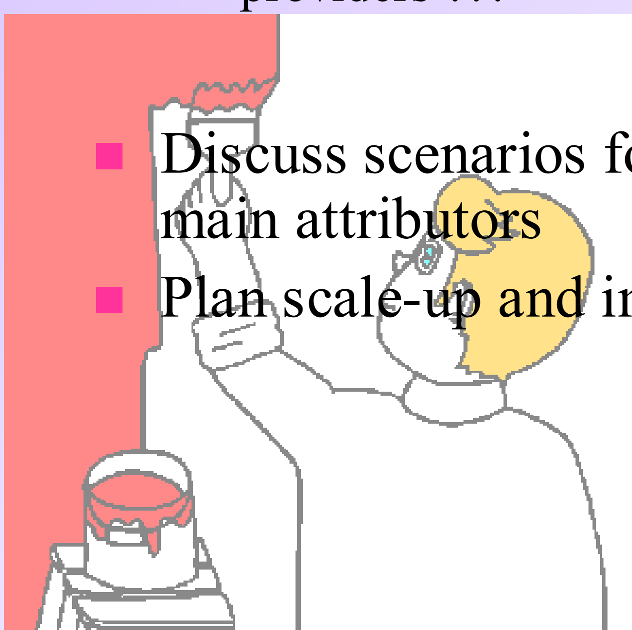
Carburization Resistance Coating Market (cont)

- Petrochemical Industry
  - Ethane/propane to Ethylene cracking (pyrolysis)
  - Gas-to-Liquid (GTL) – e.g., **Syntroleum**
  - Hydrocracking and hydrotreating plants (also H_2 consumers)
  - Heavy oil to light fuel (growing trend-consuming H_2)
- Coal and gas based electrical power generation
- Other Applications
  - Many other high-temperature corrosion resistance applications for steel and stainless steel industrial applications
    - Heat exchangers, engines, pipes, construction materials



Implementation Plans
Marketing plans

- Discuss plant maintenance and infrastructure management with
  - SMR, gasification, Syngas users, and hydrocracking companies
- Identify the main attributors for plant design and maintenance
  - Plant design construction companies, maintenance service providers, materials producers, Plant fabricators, paint companies, coating service providers ???



Who is in charge?

- Discuss scenarios for coating technology development with main attributors
- Plan scale-up and implementation with main attributors

Summary

- Preceramic polymer (PHMS) + fillers make <u>very inexpensive</u> composite coatings with wide range of control over processing and characteristics.
  - Versatile chemistry for processing, composition, microstructure, and property tailoring.
  - Reactive fillers can
    - Expand – compensating the polymer shrinkage.
    - Undergo "displacement" reactions with the pyrolyzed polymer.
    - Interact with steel - forming protective alloy layers (aluminides).
- Easy air-stable handling and processing (like paint)
- Simple paint, spray or dip coating techniques
- Excellent wetting and adherence to metals
- Simple pyrolysis cycle in air, argon or nitrogen
- Multiple and graded coatings are feasible.

Summary (cont)

- Broad range of ceramic and metal-ceramic composite coatings with significant density
  - Coatings with excellent integrity obtained with SiC- and $TiSi_2$-filled coatings.
    - Preliminary evaluation shows good response to thermal cycling.
- Diffusion-reaction coatings are feasible with Al as a filler.
  - Forming Iron Aluminide
- Carburization resistance coatings are of high need for major energy producing and energy saving industries.
- Other high-temperature protective coatings are also envisioned.

Acknowledgements

- **DOE/Industrial Technology Program**
  - Dr. Sara Dillich
  - Dr. Charles Sorrell

- **Industrial Partners**
  - Dr. Eric Minford; Air Products and Chemicals, Inc.
  - Dr. Jeff Price; Solar Turbines
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